The Lattice Energy of Nitrogen Pentoxide

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Introduction

As an ionic crystal N_2O_5 is unusual in several respects. It possesses a layer structure in which each ion is surrounded by only three neighbors of opposite charge rather than the more usual coordinations sphere of six or eight neighbors. The heat of formation is quite small, the vapor pressure is high (50mm at 0°C) and the gaseous molecule is covalent rather than ionic. These factors plus the possible effects of charge distribution within both cation and anion indicate N_2O_5 to be a particularly interesting example for application of the ionic model of lattice energy.

The Heat of Formation of NO_3^-

In applying the Born-Haber cycle to N_2O_5 to determine the lattice energy it is found that the heat of formation of the nitrate ion is the only quantity for which an experimental value is not available. This quantity is obtained from calculated lattice energies of the alkali metal nitrates. Values ranging from -78[1] to -86[2] have been reported of which the average of -84 kcal/mole due to Ladd and Lee[2] is probably the most reliable. In all these evaluations of the nitrate ion heat of formation, a simplified crystal structure is implied in which the nitrate group is treated as a point charge ion. Although Topping and Chapman[3] considered NO_3^- as $N^{+5}O_3^{-2}$ in $NaNO_3$ we have felt it desirable to consider a variable charge distribution in at least one case, $CsNO_3$, where more recent data are available.

Since the nitrate ion is not spherically symmetric, the value calculated for the heat of formation of nitrate ion from a lattice energy will depend in general on the charge distribution assigned within the ion. If the charge distribution on the ion in the crystal differs from that in the free ion, then the calculated heat of formation is likely also to be different in some degree from the true heat of formation of the free ion. Nevertheless, if the charge distribution does not change appreciably from one nitrate crystal to another, a lattice energy calculated for N_2O_5 or some other nitrate from the Born-Haber cycle should still be meaningful.

Cesium nitrate crystallizes at room temperature in a hexagonal[4] lattice but the structure has not been determined. Above 160°C it exists in a cubic modification containing eight molecules per unit cell. The structure of this form is known[5] and is the basis for calculation with later correction to 25°C. The electrostatic energy of $CsNO_3$ was computed[6] for several assumed nitrate ion charge distributions and after correcting for the electrostatic self energy of the ion the results were fitted with a second degree equation in x, the nitrogen atom charge, giving the Coulomb energy

$$E_c = -150.40 + 0.534X - 0.979X^2 \text{ K cal/mole.} \quad (1)$$

This method of calculating the Madelung energy appears to be much simpler and faster than that of deriving an analytical function of point charges and multipole terms especially with more complex structures.

Equation (1) is relatively flat between the limits $x = +1$ and $x = 0$ which correspond, respectively, to a simple resonance hybrid for the nitrate ion and to placing the unit negative charge on the oxygen atoms with a neutral nitrogen atom. The exact value assumed for the charge distribution is thus unimportant. We shall assume $x = 0.17$ based on a molecular orbital treatment[7] which leads to $E_c = -150.3$ Kcal/mole. This is almost exactly the value $E_c = -150.5$ obtained by assuming a simple monomolecular unit all of the CsCl type with interatomic distance $r = 3.89A$.

The non-electrostatic terms include the van der Waals, polarization, zero point, and repulsive energies. For the van der Waals terms Ladd and Lee[2] obtained 6.8 and 0.8 Kcal/mole corresponding to the dipole-dipole and dipole-quadrupole energies based on the simple CsCl pseudocell. A more elaborate calculation of these terms is possible but does not seem justified. We have choosen to neglect the polarization energy. A preliminary calculation in the case of N_2O_5 revealed the contribution from this term to be quite small and a similar result is expected for $CsNO_3$. For the zero point energy a value of 1 Kcal/mole is assumed.

For the compressibility, β, Ladd and Lee report a value of 4.6×10^{-12} cm^2/dyne, apparently for the cubic modification, based on data from Bridgman.[8] Our own extrapolation of Bridgman's results leads to $\beta = 5.0 \pm 0.2 \times 10^{-12} cm^2$/dyne for the room temperature (hexagonal) form and we are aware of no direct measurements on the high temperature form. However, the structural difference between the two forms of $CsNO_3$ is apparently not great [4] and there is no recourse but to apply the room temperature value of β to the cubic form. In order to correct this value of β to 167°C appropriate to the lattice parameters determination we assume a temperature coefficient $\frac{1}{\beta}\frac{d\beta}{dT} = 6 \times 10^{-4}$ deg^{-1} similar to that for the alkali halides. Accordingly, at 167°C, $\beta = 5.4 \times 10^{-12}$ cm/dyne and the repulsive energy, following the Ladd and Lee treatment[9] is 9.3 Kcal/mole. Thus at 167°C the total energy is $-150.3 - 6.8 - 0.8 + 9.3 + 1.0 + E_{th} = -147.6 + E_{th}$ Kcal where E_{th} is the thermal (vibrational) energy. Integration of the heat capacity equation given by Kelley[10] between 25 and 167°C gives the difference in heat content of 4.5 Kcal. The Debye temperature for $CsNO_3$ is probably quite small compared to 167°C so that $E_{th} \simeq 6RT = 5.7$ Kcal/mole. Using 5RT as the heat content of the gas ions at 298°C and combining terms the standard heat reaction is:

$$Cs^+(g) + NO_3^-(g) = CsNO_3(c); \quad \Delta H_{298} = -147.6 - 4.5 + 5.7 - 3.0 = \text{Kcal/mole.}$$
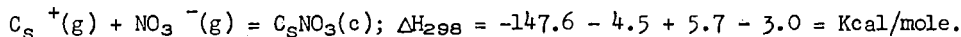
From the Born-Haber cycle using as standard heats of formation $\Delta H_f(Cs^+)$ = 110.1 Kcal[11], $\Delta H_f(CsNO_3) = -121.5$ Kcal[11,12] and the above heat of reaction, one finds $\Delta H_f (NO_3^-) = -82.2$ Kcal/mole with an estimated uncertainty of ± 1 Kcal.

If the heats of formation of $RbNO_3$ and $CsNO_3$ are revised[12] by -0.5 and -5.4 Kcal respectively, Ladd and Lee's determinations of $\Delta H_f(NO_3^-)$ become -86.5 and 85.4 Kcal/mole.

The Lattice Energy of N_2O_5

Applying the Born-Haber cycle to N_2O_5 with $\Delta H_f(NO_2^+) = 233.5 \pm 0.6$[13] $\Delta H_f(N_2O_5)c = -10.0 \pm .3$,[13] and $\Delta H_f(NO_3^-) = -82.2 \pm 1$ from above gives as the heat of formation from the gas ions at room temperature a value $\Delta H = -161.3 \pm 1.2$. This value may be taken as the lattice energy at $0°K$ with an added error not exceeding 0.5Kcal.

Based on the known structure[14] the Coulomb energy for N_2O_5 was calculated, as with $CsNO_3$, by assuming specific charge distributions in the ions NO_2^+ and NO_3^-, correcting for the self energy and fitting the results with a quadratic equation in X, the nitrate N atom charge and Y, the nitronium N atom charge. Thus:

$$E_c = -150.65 - 5.20X - 10.63Y + 2.278X^2 + 1.694XY - 1.520Y^2. \quad (2)$$

There is evident in equation (2) a far greater dependence on charge distribution than exists in equation (1). Examples of the Coulomb energy for several conceivable charge distributions are given in Table 1.

Table 1. COULOMB ENERGY OF N_2O_5

Configuration	N Atom Charge in NO_3^- (X)	NO_2^+ (Y)	Coulomb Energy E_c
Minimum value of E_c	2.02	-2.37	-143.3
Point charges	-1	1	-157.0
Neutral nitrogen	0	0	-150.7
Resonance bond	1	1.67	-172.7
Molecular Orbital[7]	0.17	0.58	-158.0

The minimum value of E_c, while having no apparent physical significance, indicates the least energy that can be associated with this particular hexagonal structure. The most reliable result is probably that from quantum mechanics, the last entry in Table 1. This energy is surprisingly close to that for the point charge configuration.

In the derivation of equation (2) it was assumed that the self energy of each ion and hence the charged distribution and interatomic distance are the same in the free state and in the crystal. It is quite possible that a real difference exists for the ions in these two states. There is evidence,[15] for example, of a charge shift in the nitrate ions of molten alkali metal

nitrates depending on the cation polarizability and an even greater shift is expected in going to the isolated ion. Unfortunately no quantitive estimate of this effect is available but it should be noted that the results leading to equation (2) indicate that a difference of only .01 units in charge between gas and crystal ions can lead to 10 Kcal difference in E_c.

Errors arrising from such effects are probably small for the nitrate ion, since its heat of formation was obtained from a lattice energy. The heat of formation of NO_2^+, however, is obtained from the ionzation potential and heat of formation of $NO_2(g)$; in this case no cancellation of error occurs. The agreement between calculated and observed heats of formation suggests that the error from this effect is probably small for both ions.

The complexity of N_2O_5 and the absence of compressibility or elastic constant data precludes any reliable calculation of the non-electrostatic terms in the lattice energy. It would be desirable to sum the repulsive energy over near pairs of atoms but repulsive parameters for N and O atoms are not well established and doubtless depend on the charge density at each atom. Estimates of the van der Waals energy face similar difficulties. In consequence only an approximation is possible. In the simple Born-Mayer expression[16] for lattice energy the total non-Coulomb contribution is given by $\rho E_c/R$ in which ρ is the exponential repulsive parameter and R is the interionic distance. The parameter ρ is often taken as 0.345 A, but is known[17] to range from at least 0.27 to 0.47. The minimum interionic distance in N_2O_5 between nitrogen atoms of the two ions is 3.12A for R. This is doubtless too small and a more effective value for R is the sum of the ion radii following Kapustinskii[18] Taking $r(NO_2^+) = 1.3A$ from Grison et al[14] and $r(NO_3^-) = 1.9A$ from Waddington[18] gives $.345E_c/R = 17$ Kcal. This estimate is still likely to be too large in that it tends to estimate the repulsive energy rather than the total non-Coulomb energy. In the case of C_aIO_3 a similar estimate exceeds the sum of the repulsive and van der Waals energies by a factor nine. An examination of the alkali halides reveals a gradual cancellation of the repulsive and van der Waals terms as the ion sizes increase until with C_sI the sum of these two terms is nearly zero. Since the ions in N_2O_5 approximate in size to the heavier alkali and halide ions it would appear that here too there is likely a near cancellation of non-electrostatic terms. The principal evidence that the non-electrostatic energy is small in N_2O_5, however, is the close agreement between the experimental lattice energy of -161 Kcal and the Coulomb energy valves in Table 1.

It was remarked earlier that an approximate calculation had been made of the polarization energy in N_2O_5. This estimate is well under 1 Kcal/mole and thus polarization may be neglected. The sum of the repulsion and dispersion energies, based on the preceeding comments, is not likely to exceed 10 Kcal and may be much smaller. As an estimate we take 5 ± 5 Kcal. Equating the lattice energy to the thermal value indicates a required Coulomb energy of $E_c = -166 \pm 5$ Kcal/mole. In terms of equation (2) this value for E_c cannot be used to establish a unique charge distribution but leads to rather broad limits such as $X = 0$, $Y = 1.2 \pm 0.4$ or $X = 1$, $Y = 1.1 \pm 0.4$. The most reliable assignment of charge is that from quantum mechanics and the value of E_c from this charge assignment, -158 Kcal/mole in Table 1, is close to the required range of -166 ± 5 Kcal/mole.

In view of the possibility of a significant energy difference associated with the free and lattice bound ions this agreement is quite satisfactory.

Acknowledgment

References

1. D. F. C. Morris, J. Inorg. Mec. Chem. 6, 295 (1958).

2. M. F. C. Ladd and W. H. Lee, J. Inorg. Nuc. Chem. 13, 218 (1960).

3. J. Topping and S. Chapman, Proc. Roy. Soc. A113, 658 (1927).

4. L. Waldbauer and C. C McCann, J. Chem Phys. 2, 615 (1934)

5. R. W. G. Wyckoff, 'Crystal Structures' V2, 2nd ed., 1964; John Wiley and Sons, Inc.

6. The I. B. M. 7090 Madelung constant program was kindly provided by Dr. Q. Johnson of Laurence Radiation Labs., Livermore, California. It was adopted for 7040 operation by Dr. J. H. Schachtschneider.

7. F. S. Mortimer, pvt. communication.

8. P. W. Bridgman, Proc. Am. Acad. Arts Sci. 76, 1,9 (1945).

9. M. F. C. Ladd and W. H. Lee, Trans. Far. Soc. 54, 34 (1958).

10. K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960).

11. F. D. Rossini, Nat. Bureau Standards Circ. 500 (1950)

12. Revised by - 3.4 Kcal according to G. N. Lewis, M. Randall, K. S. Pitzer, L. Brewer, 'Thermodynamics', 2nd Ed., 1961, McGraw Hill, page 678.

13. D. D. Wagman, Nat. Bureau Standards, Rept. No. 7437 (1962).

14. E. Grison, K. Eriks, V. L. de Vries, Acta. Cryst. 3 290 (1950).

15. G. J. Janz and D. W. James, J. Chem. Phys. 35, 739 (1961).

16. Waddington, T. C. 'Lattice Energies' in Adv. Inog. Chem. and Radiochem. 1 (1959)

17. E. C. Baughan, Trans. Far. Soc. 55, 736 (1959).

18. A. F. Kapudtinskii, Quart. Rev. 10, 283 (1956).